

Preparation of Polydimethylsiloxane Nanolatices by Emulsion Polymerization in a Water–Aminoethanol System

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ABSTRACT: Stable and translucent polydimethylsiloxane nanolatices in a water–aminoethanol (AE) system were prepared by the emulsion polymerization of octamethylcyclotetrasiloxane (D_4) with nonionic polyoxyethylene alcohol ethers and polyoxyethylene aryl ether as surfactants and with KOH as an initiator. The effects of the AE concentration on the emulsion polymerization rate (R_p) of D_4 and the physical properties of the resultant nanolatices were investigated. Increasing the AE concentration in the reaction mixture dramatically increased the emulsion R_p value of D_4 , and the kinetics of the D_4 emulsion polymerization in this system were consistent with the Morgan–Kaler theory of microemulsion polymerization. When the AE concentration in the emulsion increased, the transparency value of the resultant emulsion increased, and the size of the droplets in the re-

sultant nanolatices decreased. In addition, the molecular weight of the polysiloxane in the resultant emulsion also increased with the increase in the AE concentration in the reaction mixture. A nanolatex prepared by the emulsion polymerization of 0.98M D_4 with 185 g/L AE had a transparency value of 80.9% and a mean diameter of 59.5 nm. The morphology of polysiloxane nanolatices cured with (*N,N*-diethylaminomethyl)-triethoxysilane was observed with transmission electron microscopy, and the size of the globular particles was consistent with that obtained by dynamic light scattering. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 347–352, 2005

Key words: emulsion polymerization; polysiloxanes; silicones

INTRODUCTION

Polysiloxanes and silicones have been an interesting subject because of their novel physical and chemical properties, including good electrical isolation, good thermal stability, extremely low surface tension, and water vapor permeability. For example, polysiloxane oils are widely used in industry as release materials, antifoam agents, textile finishing agents, medical additives, lubricants, and mechanical fluids in a number of products such as cosmetic preparations and polishes.^{1–4} If possible, they are used in the form of a water emulsion rather than in the form of an organic solution for environmental reasons. Usually, polysiloxane emulsions are prepared by emulsification and emulsion polymerization in which cationic, anionic, or nonionic surfactants or their mixtures are used as the emulsifiers. Emulsion and microemulsion polymerizations are also convenient methods for the preparation of translucent polysiloxane nanolatices with narrow particle size distributions. However, most of the work relating to the prepara-

tion of polysiloxanes and silicones via emulsion polymerization appears in patents, and little work has been published about the kinetics and mechanism of siloxane emulsion polymerization, especially in a nonionic emulsion polymerization system.^{5–12} In some cases, such as the areas of medical and personal care, a nonionic polysiloxane emulsion is more compatible than an ionic one. It has been reported that in a nonionic emulsion polymerization system, the emulsion polymerization rate (R_p) of cyclosiloxane monomer is slower and the molecular weight of the resultant polysiloxane is smaller in comparison with that prepared via ionic means.³

In a previous study,¹³ we reported the preparation of polysiloxane nanolatices by the microemulsion polymerization of octamethylcyclotetrasiloxane (D_4) with nonionic polyoxyethylene alcohol ether and polyoxyethylene aryl ether surfactants as emulsifiers and with ethylene glycol (EG) as a cosurfactant. R_p of D_4 in the presence of EG was faster than that in the absence of EG, and the kinetics of D_4 emulsion polymerization obeyed the Morgan–Kaler microemulsion polymerization theory.¹⁴ It was also preliminarily found that, when aminoethanol (AE) was added to the reaction mixture, the emulsion R_p value of D_4 increased.

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To address the role of AE in D_4 emulsion polymerization, we studied the preparation of polydimethylsiloxane nanolatices by the nonionic emulsion polymerization of D_4 in a water–AE system. The effects of the AE amount added to the reaction mixture on the emulsion R_p value of D_4 and the physical properties as well as the number-average molecular weight (M_n) of the polydimethylsiloxane in the resultant emulsion were investigated in detail.

EXPERIMENTAL

Materials

D_4 from GE Toshiba Silicones (Tokyo, Japan) with 99% purity and polyoxyethylene nonylphenol ether (NP-40) with a polymerization degree of $-\text{CH}_2\text{CH}_2\text{O}-$ (EO) of 40, polyoxyethylene (EO = 15) lauryl ether (AEO-15), and polyoxyethylene (EO = 25) stearyl ether (PPJ-O) from Jinling Petrochemical, Ltd., Corp. (Nanjing, China), were used as received. Potassium hydroxide (82%), acetic acid (99.5%), ethanol (99.5%), and toluene (99.5%) were all chemically pure reagents from Nanjing Chemical Reagent Factory (Nanjing, China) and were used as received. AE from Beijing Chemical Factory (Beijing, China; 98%) was a chemically pure reagent and was used as received. (*N,N*-Diethylaminomethyl)-triethoxysilane (DEMS; 95%) was received from Mingtian Chemical, Ltd., Corp. (Liyang, China), and was distilled under reduced pressure before use.

Preparation of the polysiloxane nanolatices

Polysiloxane nanolatices were prepared by the emulsion polymerization of D_4 . For example, 78.0 g of D_4 , 13.5 g of PPJ-O, 7.5 g of NP-40, 6.0 g of AEO-15, 20.0 g of AE, and 130.0 g of distilled water were added into a 500-mL, four-necked, glass flask equipped with a reflux condenser, a thermometer, and a stirrer. When the reaction system was heated to 80°C, 12.5 g of a 20.0 wt % potassium hydroxide aqueous solution was added to the system, and the reaction mixture was stirred at a temperature of $80 \pm 0.5^\circ\text{C}$. At the desired polymerization time, about 1 g of the reaction sample was taken out of the flask with a burette, cooled to room temperature, and weighed with an analytical balance. KOH in the specimen was neutralized with a calculated amount of a 5.0 wt % acetic acid aqueous solution and dried in an oven at 150°C for 2 h. The fractional conversion of D_4 (f) was calculated according to a gravimetric method.

After 8 h, the emulsion polymerization reaction was ended by the addition of 10.5 g of a 25.0 wt % acetic acid aqueous solution, and the resultant emulsion was cooled to room temperature with stirring.

Measurements

The stability of the resultant polysiloxane nanolatices was studied with a centrifuge (Tianli Medical Instruments, Ltd., Jiangyan, China) at a speed of 3000 rpm for 30 min.

The transparency of the polysiloxane emulsion was measured with a visible spectrophotometer (722S, Shanghai Analytical Instrument Factory, Shanghai, China) with incident light at a wavelength of 580 nm, and distilled water was used as a reference with a transparency value of 100%.

The size and size distribution of the polysiloxane nanolatices were determined by dynamic light scattering (90 Plus, Brookhaven Instrument Corp., Huntsville, NY) at a fixed angle of 90° and at a temperature of 25°C. The size distribution was given by the polydispersity index.

To measure M_n of the polydimethylsiloxane in the resultant emulsion after polymerization, the polysiloxane was precipitated from the emulsion with ethanol, washed with an excess amount of ethanol three times, and then dried in an oven at 120°C for 8 h to remove water, ethanol, and low-molecular-weight siloxanes. The intrinsic viscosity ($[\eta]$) of the resultant polysiloxane was measured with toluene as the solvent in a constant-temperature bath at $25 \pm 0.2^\circ\text{C}$ with an Ubbelohde viscometer (Zhejiang Hongda Chemical & Instrument, Ltd., Co., Hangzhou, China). M_n was calculated via Berry's relationship between $[\eta]$ and M_n .¹⁵

Transmission electron microscopy (TEM) was performed on a JEOL JEM-200CX (Akishima, Tokyo, Japan). To crosslink the polydimethylsiloxane in the nanolatex droplets for TEM analysis, 10 mL of the polysiloxane emulsion was diluted with 20 mL of distilled water, and 10 mL of a 3.0 wt % DEMS aqueous solution was added to the diluted emulsion under stirring at room temperature; then, this mixture was stored at room temperature for 1 week. Before the TEM measurements, the DEMS-crosslinked emulsion was diluted with three volumes of distilled water, placed onto a copper grill covered with nitrocellulose, dried at room temperature for 48 h, and then stained with a 1.0% (w/v) sodium phosphotungstate aqueous solution.

RESULTS AND DISCUSSION

Kinetics of the siloxane emulsion polymerization in a water–AE system

In this study, the emulsion polymerization of D_4 was carried out in a $\text{H}_2\text{O}/\text{AE}$ system. The emulsion R_p values of D_4 with different AE concentrations were measured, and f versus the polymerization time is presented in Figure 1. Figure 1 shows that the emulsion R_p value of D_4 increased with an increase in the

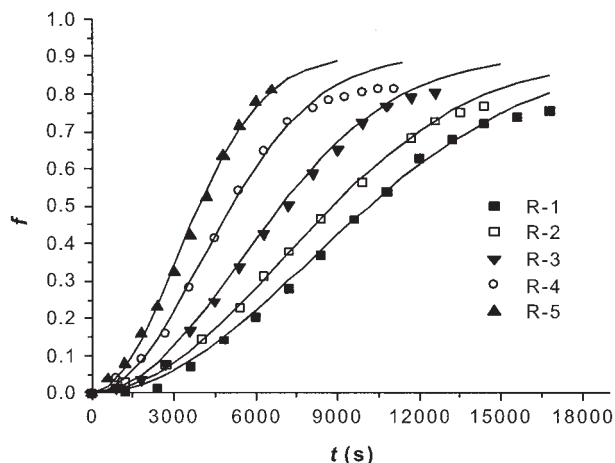


Figure 1 Experimental f values of D_4 versus t with different AE concentrations in the reaction system. The solid lines are the fit of eq. (1) to data with chosen A values of 1.58×10^{-8} , 2.10×10^{-8} , 3.40×10^{-8} , 6.20×10^{-8} , and 1.04×10^{-7} for reactions R-1 to R-5, respectively (for R-1 to R-5, $[D_4] = 0.98M$, $[PPJ-O] = 50$ g/L, $[NP-40] = 27.8$ g/L, $[AEO-15] = 22.2$ g/L, $[KOH] = 0.165M$, and temperature = $80^\circ C$; $[AE] = 0$ for R-1, 37.0 g/L for R-2, 74.0 g/L for R-3, 130.0 g/L for R-4, and 185.0 g/L for R-5).

AE concentration in the reaction mixture. At $[AE] = 0$, the conversion of D_4 was only 0.72 after 5 h of polymerization. However, at $[AE] = 74.1$ g/L, $[AE] = 130.0$ g/L, and $[AE] = 185$ g/L in the emulsion, the reaction attained equilibrium after 3.6, 2.9, and 1.7 h, respectively. f was fitted with the following equation, which represents the kinetics of the microemulsion polymerization of D_4 :

$$f = 0.9 - 0.9 \times \exp(-At^2/2) \quad (1)$$

where t is the reaction time, A is a parameter determined by the reaction conditions, and the factor 0.9 is the maximum conversion of D_4 after emulsion polymerization.¹³

With eq. (1), the solid lines in Figure 1 were drawn with chosen A values of 1.58×10^{-8} , 2.1×10^{-8} , 3.40×10^{-8} , 6.20×10^{-8} , and 1.04×10^{-7} for reactions R-1 to R-5, respectively. The kinetics of the emulsion polymerization of D_4 in the H_2O/AE system are consistent with eq. (1).

Under the same reaction conditions, R_p of D_4 in the H_2O/AE system was investigated with different KOH molar concentrations in the emulsion, and R_p of D_4 versus the KOH concentration is shown in Figure 2. From Figure 2, we find that R_p increases when the KOH concentration is increased in the emulsion. The experimental data were also fitted with eq. (1) with chosen A values of 3.64×10^{-8} , 6.20×10^{-8} , and 1.72×10^{-7} for R-6, R-4, and R-7, respectively, as the solid lines in Figure 2.

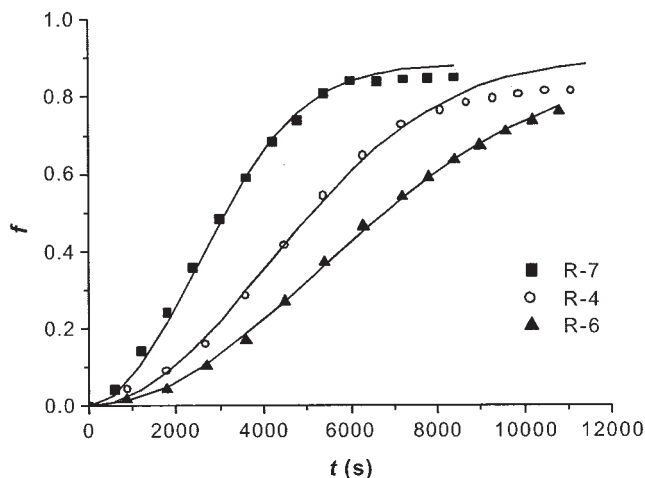


Figure 2 Experimental f values of D_4 versus t with different KOH concentrations in the reaction system. The solid lines are the fit of eq. (1) to data with chosen A values of 3.64×10^{-8} , 6.20×10^{-8} , and 1.72×10^{-7} for reactions R-6, R-4, and R-7, respectively (for R-6, R-4, and R-7, $[D_4] = 0.98M$, $[PPJ-O] = 50.0$ g/L, $[NP-40] = 27.8$ g/L, $[AEO-15] = 22.2$ g/L, $[AE] = 130.0$ g/L, and temperature = $80^\circ C$; $[KOH] = 0.132M$ for R-6, 0.165M for R-4, and 0.198M for R-7).

These results suggest that the kinetics of the D_4 emulsion polymerization in the H_2O/AE system shows behavior similar to that of microemulsion polymerization.^{13,14}

Effect of the AE concentration on the physical properties of the polysiloxane emulsion

The stability of the resultant polysiloxane emulsions with different AE concentrations was studied with a centrifuge at a speed of 3000 rpm for 30 min, and it was found that there were no floaters or precipitates in the sample after the test.

The physical properties of the resultant polysiloxane emulsions of R-1 to R-5, such as the transparency value, particle size, and size polydispersity, were studied, and the results are displayed in Table I and Figures 3 and 4, respectively.

TABLE I
Relationship Between the AE Concentration and the Physical Properties of the Resultant Emulsion

	[AE] (g/L)				
	0	37.0	74.0	130.0	185.0
Transparency (%) ^a	0.7	1.7	7.8	27.8	80.9
D (nm) ^b	79.3	67.1	62.1	59.2	59.5
Polydispersity of D ^b	0.199	0.225	0.184	0.151	0.190

^a Measured with a visible spectrophotometer.

^b Determined by dynamic light scattering.

The transparency value of the resultant nanolatex increased as AE was added to polydimethylsiloxane. When the added amount of AE was less than 75 g/L, the final emulsion showed a milklike, opaque liquid. However, when the added amount of AE was more than 75 g/L in the emulsion, the final emulsion was a translucent, viscous liquid. The transparency of the resultant polysiloxane emulsion versus the amount of added AE is shown in Figure 3. The transparency value of the polysiloxane emulsion only increased from 0.7 to 7.8% when the AE concentration increased from 0 to 74.0 g/L; however, it increased dramatically from 7.8 to 80.9% when the AE concentration increased from 74.0 to 185.0 g/L in the emulsion.

Meanwhile, the effects of the AE concentration on the particle size and size polydispersity of the droplets in the resultant polysiloxane emulsion were investigated with dynamic light scattering, and the results are shown in Figure 4 and Table I. From Figure 4, we find that the mean diameter (D) of the polysiloxane droplets without the addition of AE to the reaction system was 79.3 nm, but D of the polysiloxane droplets decreased to 67.1, 62.1, and 59.2 nm when the amount of added AE was 37.0, 74.0, and 130.0 g/L in the polysiloxane emulsion, respectively, and D remained at 59.5 nm when the AE concentration increased to 185.0 g/L. In addition, the effect of the AE concentration in the reaction mixture on the polydispersity of D of the droplets was weak, and the polydispersity of D remained between 0.225 and 0.151, as shown in Table I.

These results mean that adding AE to the emulsion increases the transparency value of the resultant polysiloxane emulsion and decreases the particle size of the polysiloxane droplets in the resultant emulsion. Thus, AE seems to have the same effect as that of a cosurfactant.

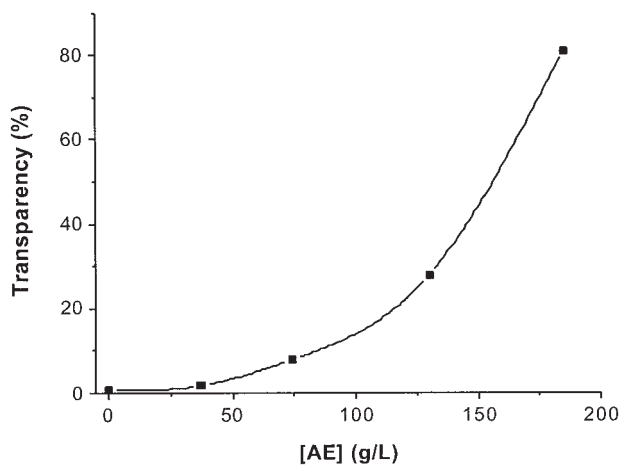


Figure 3 Variation of the transparency value of the polysiloxane emulsion with different AE concentrations in the reaction system.

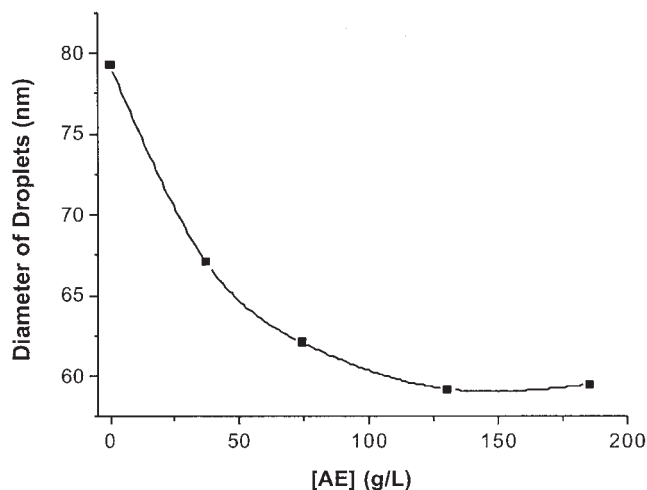


Figure 4 Particle size of the droplets in the polysiloxane nanolatex with different AE concentrations in the reaction system.

Effect of the AE concentration on the molecular weight of the polysiloxane in the emulsion

As mentioned in earlier works,^{3,7,13} M_n of polysiloxane made by nonionic emulsion polymerization is related to the reaction temperature and is usually about 20,000 after polymerization at 80°C for 8 h; this is lower than M_n of polysiloxane made by ionic emulsion polymerization under the same reaction conditions.

For comparison with ionic emulsion polymerization, the molecular weight of polysiloxane made by nonionic emulsion polymerization in the water-AE system was studied with different AE concentrations under the same reaction conditions, and the results are shown in Figure 5. When the AE concentration in-

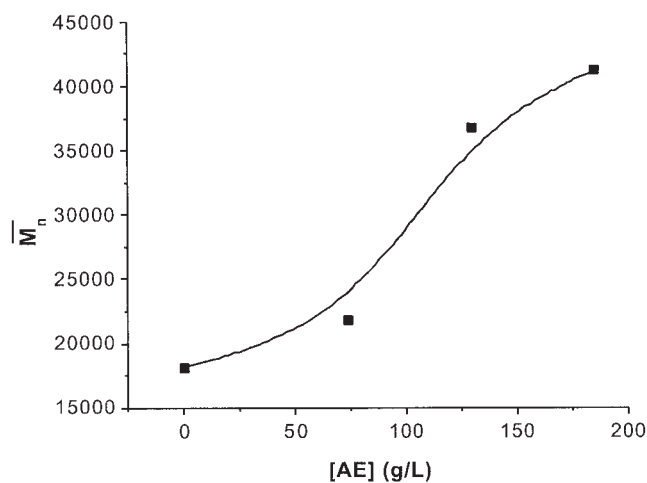


Figure 5 M_n of polydimethylsiloxane in the resultant nanolatex with different AE concentrations in the reaction system.

creased in the emulsion, M_n of polysiloxane in the resultant emulsion increased. With no AE in the emulsion, M_n of polysiloxane in the emulsion after 8 h of emulsion polymerization was about 18,000. When the AE concentration was 74.0, 130.0, and 185.0 g/L in the emulsion, M_n of the polysiloxane reached 22,000, 37,000, and 41,000, respectively.

It was reported that, in an ionic emulsion polymerization of D_4 , at the beginning of the emulsion polymerization, D_4 was polymerized to low-molecular-weight hydroxyl-terminated polydimethylsiloxanes. Then, during the second stage of the emulsion polymerization, the low-molecular-weight polysiloxanes condensed with one another to produce high-molecular-weight polysiloxanes.^{7,10–12} We think that the reaction process is the same in this work. As mentioned previously, R_p of D_4 in the lower AE concentration system was slower than that in the higher AE concentration system, and it was expected that the condensation rate of low-molecular-weight polysiloxanes to high-molecular-weight polysiloxanes would be slower in the lower AE concentration system; thus, the condensation time of low-molecular-weight polysiloxanes to high-molecular-weight polysiloxanes was longer. In the lower AE concentration system, the condensation reaction did not attain equilibrium after 8 h at 80°C; therefore, M_n of the polydimethylsiloxane in the resultant emulsion was lower.

TEM photography of the crosslinked nanolatex droplets

To investigate the shape and size of the droplets in the polysiloxane nanolatex, TEM measurements were carried out. The polysiloxane in the emulsion was a viscous liquid and coalesced after the removal of the water. Thus, it should have been cured before measurement by TEM. In a previous article,¹³ polyvinylmethylsiloxane was introduced into polydimethylsiloxane chains, and the polydimethylsiloxane was crosslinked with $K_2S_2O_8$. However, in this study, it was difficult to polymerize the vinyl group with $K_2S_2O_8$ in the H_2O/AE system. A water-soluble silane, DEMS, was used as the crosslinking agent. When DEMS was added to the polysiloxane emulsion, it reacted quickly with $HO-Si\equiv$, the end group of polydimethylsiloxane in the emulsion droplets, and the polysiloxane in the emulsion droplet was cured after being dried. Thus, the shape of the droplets was fixed.

Figure 6 shows a TEM photograph of the cured polydimethylsiloxane nanolatex after it was stained with sodium phosphotungstate. As shown in Figure 6, the particles were globular. The diameter of the globular droplets of silicone in the nanolatex mostly ranged between 20 and 150 nm, with a mean size of 60

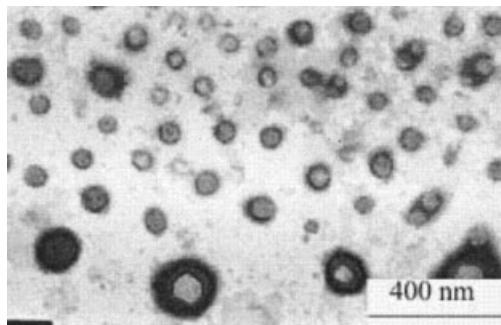


Figure 6 TEM image of polysiloxane nanolatex polymerized in the H_2O/AE system.

nm; this result is consistent with that obtained by dynamic light scattering, as listed in Table I. Some particles with a diameter greater than 150 nm could be attributed to the coalescence of two or more droplets, with a diameter of about 60 nm each, during crosslinking and drying. Thus, the polydispersity of the particle size via TEM was larger than that obtained by dynamic light scattering.

Additionally, the particles in the TEM image show a white–black core–shell structure depending on the staining time and size of the particles. This is because the crosslinking agent, DEMS, was enriched on the surface of the polysiloxane droplets and the amino group of the crosslinking agent was easily stained with sodium phosphotungstate.

CONCLUSIONS

Stable and translucent polydimethylsiloxane nanolatices in a water–AE system were prepared via the emulsion polymerization of D_4 with nonionic polyoxyethylene alcohol ether and polyoxyethylene aryl ether as surfactants and with KOH as the initiator. The effects of the AE concentration on the emulsion R_p value of D_4 and the physical properties of the resultant emulsion were investigated. Under the same reaction conditions, increasing the AE concentration in the reaction mixture dramatically increased the emulsion R_p value of D_4 . The kinetics of the siloxane emulsion polymerization in this system were consistent with the Morgan–Kaler theory of microemulsion polymerization. When the AE concentration in the emulsion increased, the transparency value of the resultant emulsion increased, the particles size of the droplets in the resultant emulsion decreased, and M_n of the polysiloxane in the resultant emulsion increased after polymerization at 80°C for 8 h. The polysiloxane in the nanolatex cured with DEMS was analyzed via TEM after staining with sodium phosphotungstate; the particles were globular, and the size of the particles was

consistent with that obtained by dynamic light scattering.

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